

## 5 SELECTIVE HYDROGENATION CATALYST

Background of Invention

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This invention relates to a catalyst useful for selective hydrogenation of unsaturated compounds, such as acetylene, in an olefinic feed stream, particularly for front-end ethylene purification. This invention also  
15 relates to a process for the preparation of the catalyst and the use of the catalyst for the selective hydrogenation of unsaturated compounds, such as acetylene, particularly for front-end ethylene purification.

The manufacture of unsaturated hydrocarbons usually  
20 involves cracking various types of hydrocarbons and often produces a crude product containing hydrocarbon impurities that are more unsaturated than the desired product. These unsaturated hydrocarbon impurities are often very difficult to separate by fractionation from the desired  
25 product. An example of this problem occurs with ethylene purification, in which acetylene is a common impurity. It is often difficult, industrially, to remove undesirable, highly unsaturated hydrocarbons by hydrogenation without significant hydrogenation of the desired hydrocarbons.

30 Two general types of gas phase selective hydrogenation processes for removing undesired, unsaturated hydrocarbons are commonly used. One type, known as "front-end" hydrogenation, involves passing the

5 crude gas from the initial cracking step, after removal of  
steam and condensible organic material, over a  
hydrogenation catalyst. The crude gas has a large  
hydrogen content relative to the quantity of acetylenes  
present, thereby, theoretically making possible the  
10 hydrogenation of all of those acetylenes as well as a  
substantial quantity of the ethylene that is present. In  
practice, substantially complete hydrogenation of the  
acetylenes with sufficient selectivity to produce olefins  
of polymerization quality is often a problem. The high  
15 concentration of hydrogen present in the front-end systems  
results in the need for a very selective catalyst that  
does not also substantially hydrogenate desirable  
components of the feed stream, such as ethylene.  
Overhydrogenation can lead to a thermal excursion in  
20 reactors, which is also known as "run-away". Under  
"run-away" conditions, excessively high temperatures are  
experienced, severe loss of ethylene occurs, and catalyst  
damage takes place. Another problem that can occur in a  
front-end reactor system is a furnace upset which can  
25 result in swings in the CO concentration from moderate  
levels to very low levels. Conventional, front-end  
catalysts cannot tolerate these large swings in CO  
concentration very well which often produce "run-away"  
conditions.

30 In the other type of gas phase selective  
hydrogenation, which is known as "tail-end" hydrogenation,

5 the crude gas is first fractionated and the resulting concentrated product streams are individually reacted with hydrogen in a slight excess over the quantity required for hydrogenation of the undesirable, highly unsaturated hydrocarbons, such as acetylene. However, in tail-end  
10 processes there is a greater tendency for deactivation of the catalyst, and consequently, periodic regeneration is necessary. While thermal excursion is not a concern, formation of undesirable polymers is often a major problem.

15 A number of patents have discussed selective hydrogenation of unsaturated hydrocarbons, such as U.S. Patent Nos. 4,126,645, 4,367,353, 4,329,530, 4,347,392 and 5,414,170. The catalysts that are preferred for selective hydrogenation reactions conventionally utilize palladium,  
20 supported on an alumina substrate, as disclosed, for example, in U.S. Patent Nos. 3,113,980, 4,126,645 and 4,329,530. Other gas phase, palladium on alumina catalysts for the selective hydrogenation of acetylene compounds are disclosed, for example, in U.S. Patent Nos.  
25 5,925,799, 5,889,138 and 5,648,576.

One of the problems with conventional palladium on alumina catalysts is that under normal operating conditions not only is the acetylene hydrogenated, a substantial proportion of the ethylene is also converted  
30 to ethane. In addition, the palladium on alumina catalysts often have relatively low stability due to the

5 formation of large quantities of oligomers on the catalyst surface during the selective hydrogenation process.

To overcome these problems, promoters or enhancers are added to the catalyst. One common enhancer for a conventional palladium on alumina selective hydrogenation  
10 catalysts is silver. Acetylene hydrogenation catalysts for ethylene purification comprising palladium and silver on a support material are disclosed in U.S. Patent Nos. 4,404,124, 4,484,015, 5,488,024, 5,489,565 and 5,648,576.

Catalysts comprising palladium, silver, an alkali  
15 metal fluoride and a support material, which are utilized for the hydrogenation of feed stream impurities, such as dienes and diolefins, are disclosed, for example, in U.S. Patent No. 5,489,565.

Catalysts useful for hydrogenation of organic  
20 compounds are also disclosed in U.S. Patent Nos. 6,255,548 and 6,294,696 and comprise at least one support, at least one metal from Group VIII, and at least one additional element, M, selected from the group consisting of germanium, tin, lead, rhenium, gallium, indium, gold,  
25 silver and thallium, preferably tin or germanium. The catalyst for this process is prepared by introducing a metal into an aqueous solvent, preferable in the form of an organometallic compound containing at least one carbon-M bond. See also U.S. Patent Nos. 3,962,139 and  
30 6,225,516.

5 U.S. Patent No. 6,465,391 discloses a selective hydrogenation catalyst and processes for the production thereof, wherein the catalyst comprises an inorganic support material, a palladium component, a silver component, and a promoter component having the formula  
10  $XYF_n$ , where an X is an alkaline metal, Y is an element selected from the group consisting of antimony, phosphorous, boron, gallium, aluminum, indium, thallium, and arsenic and n is an integer which makes  $YF_n$  an monovalent anion.

15 U.S. Patent No. 3,992,468 discloses a process for hydrodealkylating alkylaromatic hydrocarbons using a catalyst comprising two metals, the first of the metals selected from the group consisting of cobalt, ruthenium, osmium, palladium, rhodium, indium, and platinum or from  
20 the group consisting of molybdenum, tungsten, and manganese, and the second metal selected from the group consisting of zinc, cadmium, gallium, indium, thallium, manganese, copper, silver, gold, yttrium, titanium, niobium, tantalum, chromium, molybdenum, tungsten,  
25 rhenium, germanium, tin and lead.

While conventional silver/palladium-based catalysts for the selective hydrogenation of acetylene have been useful, there are a number of problems that have been discovered from their use, including relatively low  
30 tolerance to carbon monoxide concentration swings and lower selectivity than is desirable by the industry.

5       The catalysts of the invention are designed to address these deficiencies in conventional ethylene purification catalysts.

          Accordingly, it is an object of this invention to disclose a process for the selective hydrogenation of an  
10   olefinic feed stream containing acetylenic impurities, particularly for ethylene purification.

          It is a further object of this invention to disclose a process for front-end selective hydrogenation of acetylenic impurities, whereby the quantity of the  
15   desirable olefins, particularly ethylene, is not substantially reduced.

          It is a further object of the invention to disclose a palladium/thallium catalyst for use in the selective hydrogenation of acetylenic impurities, particularly for  
20   use in front-end ethylene purification.

          It is a further object of the invention to disclose a palladium/thallium catalyst for selective hydrogenation of acetylenic impurities which contains precise quantities of palladium and thallium.

25       It is a still further object of the invention to disclose a palladium/thallium selective hydrogenation catalyst for the selective hydrogenation of acetylene which exhibits improved selectivity, resistance to run-away, and tolerance to CO concentration swings in  
30   comparison with conventional palladium or palladium/silver selective hydrogenation catalysts.

5        These and other objects can be obtained by the disclosed selective hydrogenation catalyst and process for the preparation and use of the selective hydrogenation catalyst for use in an olefinic feed stream containing acetylenic impurities, particularly for ethylene  
10   purification.

### **Summary of the Invention**

      The present invention is a process for the production and distribution of a catalyst for the selective  
15   hydrogenation of acetylenic impurities for ethylene purification comprising

      preparing a carrier material in a suitable shape;

      impregnating the carrier with a palladium metal source, preferably in solution;

20        calcining the palladium-impregnated carrier;

      impregnating the palladium-impregnated carrier with a thallium- metal source, preferably in solution,

      calcining the palladium/thallium impregnated carrier;  
and

25        reducing the palladium and thallium materials, wherein the quantity of the reduced palladium, by weight, including the palladium, comprises from about 0.001 to about 2 weight percent, the quantity of the reduced thallium, by weight including the thallium, comprises from  
30   about 0.001 to about 1 weight percent and wherein the

5 concentration of the palladium metal is not less than the concentration of the thallium metal.

Preferably the reduced catalyst is then sealed into shipping containers under a non-oxidizing material for shipment.

10 The present invention further comprises a palladium/thallium catalyst for front-end selective hydrogenation of acetylenic impurities comprising from about 0.001 to about 2 weight percent palladium, including the palladium, and from about 0.001 to about 1 weight  
15 percent thallium, including the thallium, on a low surface area carrier i.e. less than 100 m<sup>2</sup>/g, wherein the concentration of the palladium metal is not less than the concentration of the thallium metal. Preferably the ratio of the palladium metal to the thallium metal is 1:1 or  
20 less, more preferably about 10:1 or less.

The invention further comprises a process for the selective hydrogenation of acetylenic impurities for front-end ethylene purification comprising passing an ethylene feed stream containing acetylenic impurities over  
25 the catalyst described above.

#### **Detailed Description**

The catalyst of the invention is designed primarily for the selective hydrogenation of acetylene in admixture  
30 with ethylene, particularly for front-end processes. The feed stream for this selective hydrogenation process



5 normally includes substantial quantities of hydrogen, methane, ethane, ethylene, small quantities of carbon monoxide and carbon dioxide, as well as various impurities, such as acetylene. The goal of the selective hydrogenation process is to reduce substantially the  
10 amount of the acetylenic impurities present in the feed stream without substantially reducing the amount of ethylene that is present. If substantial hydrogenation of the ethylene occurs, thermal run-away can occur which adversely affects the catalyst. The catalyst of the  
15 invention exhibits enhanced selectivity, resistance to run-away, and better tolerance for CO concentration swings than is experienced using conventional selective hydrogenation catalysts.

The catalyst that is useful for this selective  
20 hydrogenation process is comprised of a low surface area carrier into which palladium and thallium are impregnated. The catalyst carrier is any relatively low surface area catalyst carrier manufactured from alumina, alpha alumina, zinc oxide, nickel spinel, titania, magnesium oxide,  
25 cerium oxide and mixtures thereof. In a preferred embodiment, the catalyst carrier is an alpha alumina. The surface area of the catalyst carrier is preferably from about 1 to about 100 m<sup>2</sup>/g, more preferably from about 1 to about 50 m<sup>2</sup>/g, and most preferably from about 1 to about 10  
30 m<sup>2</sup>/g. Its pore volume is from about 0.2 to about 0.7 cc/g, preferably from about 0.3 to about 0.5 cc/g.

5       The catalyst carrier can be formed in any suitable size and in any suitable shape, such as spherical, cylindrical, trihole trilobal, monolith, pellet, tablet, ring and the like. In a preferred embodiment the catalyst carrier is formed in a tablet shape with a diameter from  
10   about 3 to about 5 mm.

      Palladium can be introduced into the catalyst carrier by any conventional procedure. The presently preferred technique involves impregnating the catalyst carrier with a palladium metal source, preferably in the form of an  
15   aqueous solution of a palladium salt, such as palladium chloride or palladium nitrate, preferably palladium chloride. The extent of penetration of the palladium salt is preferably controlled by adjustment of the pH of the solution. In a preferred embodiment, the depth of  
20   penetration of the palladium salt is controlled such that approximately 90 percent of the palladium salt is contained within about 250 microns of the surface of the catalyst carrier. Any suitable method can be used to determine palladium penetration, such as is disclosed in  
25   U.S. Patent Nos. 4,484,015 and 4,404,124. After palladium impregnation, the intermediate impregnated catalyst composition is calcined at a temperature from about 400°C to about 600°C for at least one hour.

      Once the palladium-impregnated intermediate catalyst  
30   composition has been calcined, that composition is further impregnated with a thallium metal source, preferably a

5 thallium metal solution such as  $\text{HCO}_2\text{Tl}$ . The palladium/thallium impregnated catalyst material is then calcined at a temperature from about  $400^\circ\text{C}$  to about  $600^\circ\text{C}$  for at least one hour.

10 In an alternative process of manufacture, the thallium and palladium metals can be co-impregnated and then calcined. Notwithstanding, it is preferable that thallium metal source not be introduced before the source for the palladium metal.

15 While the reduction process can occur *in situ* within a front-end reactor, the metals of the catalyst are preferably reduced in a reduction furnace prior to shipment. The metal compounds contained in the thallium/palladium catalyst precursor are preferably reduced by heating the catalyst while under a reducing gas, at a temperature from about  $94^\circ\text{C}$  -  $535^\circ\text{C}$ , preferably from about  $94^\circ\text{C}$  -  $260^\circ\text{C}$  for a time sufficient to reduce the palladium and thallium metal sources. Preferable reducing gases include hydrogen, carbon monoxide and mixtures thereof. The catalyst is then cooled under a  
25 purge gas, such as nitrogen, to room temperature. Other conventional reduction processes may alternatively be used.

The amount of palladium present after reduction is from about 0.001 to about 2 weight percent, preferably  
30 from about 0.005 to about 0.05 weight percent, and most preferably from about 0.01 to about 0.03 weight percent

5 based on the total weight of the catalyst, including the  
palladium. The amount of thallium present in the catalyst  
after reduction is from about 0.001 to about 1 percent,  
preferably 0.001 to 0.03 weight percent, and most  
preferably from about 0.001 to about 0.01 weight percent,  
10 based on the total weight of the catalyst, including the  
thallium.

It has been discovered that a useful catalyst is  
produced when the concentration of palladium metal equals  
or exceeds the concentration of thallium metal with a  
15 preferable Pd:Tl ratio from 1:1 to about 100:1, a more  
preferable Pd:Tl ratio from 5:1 to about 50:1, and a most  
preferable Pd:Tl ratio from about 10:1 to about 20:1,  
calculated as metals.

Following a final drying step, the thallium/palladium  
20 containing catalyst is prepared for shipment. The  
catalyst is preferably loaded into individual containers  
under a non-oxidizing gaseous atmosphere for shipping.  
Preferable non-oxidizing gases include nitrogen, argon,  
carbon dioxide or mixtures thereof.

25 In use, the catalyst is placed in the bed of a  
reactor. If desired the catalyst can be reduced *in situ*  
as is possible in some operations. Alternatively, the  
catalyst, which has been reduced prior to shipment, is  
merely placed within a catalyst bed ready for use.  
30 Selective hydrogenation of acetylene occurs when a gas  
stream containing primarily hydrogen, ethylene, methane,

5 unsaturated impurities, such as acetylene, and minor  
amounts of carbon monoxide is passed over the catalyst of  
the invention. The inlet temperature of the feed stream  
is raised to a level sufficient to hydrogenate the  
acetylene. Generally, this temperature range is about  
10 35°C to about 100°C. Any suitable reaction pressure can  
be used. Generally, the total pressure is in the range of  
about 100 to 1000 psig with the gas hourly space velocity  
(GHSV) in the range of about 1000 to about 14000 liters  
per liter of catalyst per hour.

15 Conventional palladium/silver catalysts are often  
prone to run-away conditions, especially when the quantity  
of carbon monoxide changes dramatically during the  
reaction process. The catalyst of the invention is  
resistant to these run away conditions even when the  
20 quantity of carbon monoxide is low. Further, the catalyst  
of the invention exhibits enhanced selectivity over prior  
art catalysts. By the process of use of the catalyst of  
the invention, reduction of acetylene to a level less than  
about 1 ppm can be achieved.

25 Regeneration of the catalyst may be accomplished by  
heating the catalyst in air at a temperature, preferably  
not in excess of 500°C., to burn off any organic material,  
polymers or char.

### 30 **EXAMPLES**

#### **Example 1 (Comparative)**

5        A commercially available, palladium/alumina catalyst  
manufactured by Süd-Chemie Inc. under the product name  
G-83A is obtained. Analysis shows that the catalyst  
comprises a palladium on alumina catalyst containing 0.018  
weight percent palladium. The carrier is comprised of 99  
10 weight percent alumina. The catalyst has a BET surface  
area of 3.7 m<sup>2</sup>/g.

**Example 2 (Comparative)**

A commercially available catalyst manufactured by  
15 Süd-Chemie Inc. under the product name of G-83C is  
obtained. Analysis shows that the catalyst comprises a  
palladium/silver on alumina catalyst containing 0.018  
weight percent of palladium and 0.07 weight percent of  
silver on 99 weight percent alumina. The catalyst has a  
20 BET surface area of about 4.3 m<sup>2</sup>/g.

**Example 3**

A catalyst is prepared by dipping 100 grams of a  
commercially available, low surface area alumina spheres  
25 with a BET surface area of 50 m<sup>2</sup>/g in a PdCl<sub>2</sub> solution to  
yield a palladium loading of 0.03 weight percent,  
including the palladium, with a palladium depth of  
penetration that is controlled to wherein at least about  
90 percent of the palladium is within 250 microns of the  
30 surface of the spheres. After palladium impregnation, the  
intermediate catalyst is calcined at 454°C for 3 hours.

5 The palladium-containing intermediate is then impregnated with thallium in the form of  $\text{HCO}_2\text{Tl}$  to yield a thallium loading of 0.03 weight percent, including the thallium. The weight ratio between the palladium metal and the thallium metal on a by weight basis is 1:1. The catalyst  
10 containing the palladium and thallium is calcined a second time at about  $454^\circ\text{C}$  for 3 hours. The catalyst is then loaded into a reduction bed, and purged with nitrogen while the bed is heated to  $94^\circ\text{C}$ . Once this temperature is reached, the nitrogen purge gas is discontinued and  
15 hydrogen gas is introduced as a reducing gas. The bed is maintained at  $94^\circ\text{C}$  for at least 60 minutes. Upon completion of the reduction cycle, nitrogen gas is reintroduced into the bed and the bed is cooled to room temperature.

20

**Example 4**

A catalyst is prepared according to Example 3 except the low surface area alumina has a BET surface area of  $5\text{ m}^2/\text{g}$ . The catalyst is then loaded into a reduction bed,  
25 purged with nitrogen while the bed is heated to  $94^\circ\text{C}$ , and reduced as described in Example 3.

**Example 5**

A catalyst is prepared according to Example 3 except  
30 the weight ratio between the palladium metal and thallium metal was 10:1 Pd:Tl (0.03 weight percent palladium,

5 including the palladium, and 0.003 weight percent thallium, including the thallium). Further, the catalyst is not reduced.

#### **Example 6**

10 The catalyst from Example 5 is reduced as described in Example 3.

#### **Example 7**

A catalyst is prepared according to Example 6 except  
15 that the low surface area alumina has a BET surface area of 5m<sup>2</sup>/g.

#### TABLES

##### Performance Testing:

20 Table 1, which follows, provides a comparison of the performance of Examples 1 and 2 (Comparative Examples) with Examples 3 through 7. The samples are compared by passing a conventional ethylene feed stream over the catalysts. The catalysts are evaluated in a bench scale  
25 laboratory, one-half inch i.d. reactor tube, which simulated a front-end feed stock reactor.

Catalyst activity and selectivity are evaluated. For each catalyst, the inlet temperature is recorded when less than 25 ppm acetylene leakage is detected at the reactor  
30 outlet. This temperature, T<sub>1</sub>, is designated as the lower reaction temperature for catalyst activity. The inlet



5 temperature is then increased until "run-away" is observed. "Run-away" or thermal excursion is defined as a greater than 4 percent  $H_2$  loss in the system, and occurs when the hydrogenation of ethylene ( $C_2H_4$ ) is significant. The temperature of the reactor inlet when run-away is  
10 noted is reported as  $T_2$ . The catalyst activity then is evaluated in terms of the temperature range over which the catalyst could effectively function, or the temperature at which hydrogenation is first observed ( $T_1$ ) to the temperature at which run-away occurs ( $T_2$ ). A large delta T  
15 ( $T_2 - T_1$ ) indicates that the catalyst can operate effectively over a broad temperature range.

As the reactor temperature is increased, the hydrogenation reaction becomes more active with a greater amount of  $C_2H_2$  being hydrogenated and hence, removed from  
20 the product stream. However, some hydrogenation of  $C_2H_4$  also occurs indicating a loss of selectivity for the reaction. As shown in Table I, "selectivity" of each catalyst is reported as a percentage and is determined by the following calculations: 100 times (inlet  $C_2H_2$  - outlet  
25  $C_2H_2$ ) minus ( $C_2H_4$  outlet minus  $C_2H_4$  inlet) / ( $C_2H_4$  inlet minus  $C_2H_4$  outlet) times 100. Higher positive percentages indicate a more selective catalyst. Data was obtained at a moderate GHSV (7000).

30 **TABLE I**

Table I - 7000 GHSV activity/selectivity test

5

Run	Catalyst	T <sub>1</sub> (°C)	T <sub>2</sub> (°C)	Activity Range T <sub>2</sub> -T <sub>1</sub>	Selectivity at T <sub>1</sub>
Comparative Example 1	(G83A) Pd/Al <sub>2</sub> O <sub>3</sub> no pre-reduction	60	66	6	+3%
Comparative Example 2	(G83C) Pd/Ag/Al <sub>2</sub> O <sub>3</sub> no pre-reduction	46	52	6	-125%
Example 3	1:1 Pd:Tl (0.03%Pd, 0.03%Tl) on alumina 50 m <sup>2</sup> /g S.A. (reduced)	46	58	12	-41.8%
Example 4	1:1 Pd:Tl (0.03%Pd, 0.03%Tl) on alumina 5 m <sup>2</sup> /g S.A. (reduced)	37	57	20	+34%
Example 5	10:1 Pd:Tl (0.03%Pd, 0.003% Tl) on alumina (50 m <sup>2</sup> /g S.A.) (No pre- reduction)	44	58	14	+46.6%
Example 6	10:1 Pd:Tl (0.03%Pd, 0.003%Tl) on alumina (50 m <sup>2</sup> /g S.A.) (reduced)	67	84	17	+79%
Example 7	10:1 Pd:Tl (0.03%Pd, 0.003%Tl) on alumina (5 m <sup>2</sup> /g S.A.) (reduced)	58	77	19	+41.7%

10            Comparison of the activity range and the selectivity  
for the prior art catalysts (Examples 1 - 2) to the  
inventive catalysts (Examples 3 - 7) demonstrates the  
enhanced performance of the catalysts of the invention.  
Selectivity is significantly improved relative to the  
15 prior art catalysts.    Further, the catalysts of the  
invention demonstrate a broader temperature range over  
which the catalysts are active for hydrogenation than the  
prior art catalysts.

#### 20    CO concentration swings

Feedstreams supplied to commercial front-end  
hydrogenation reactors can have substantial swings in CO  
concentration. This occurs when a new hydrocarbon cracker  
is brought on-line. The CO present in the feedstream acts

5 as a selectivity enhancer. If the quantity of CO drops dramatically, thermal excursion can occur with existing commercial catalyst. To predict the performance of the catalysts of the invention under this condition, a test was developed to mimic CO concentration swings which often  
 10 occur in ethylene plants. Selected catalysts are tested under CO swing test conditions. The feed consists of 0.25% C<sub>2</sub>H<sub>2</sub>, 20% H<sub>2</sub>, 247 ppm CO, 45% C<sub>2</sub>H<sub>4</sub> and 34% CH<sub>4</sub>. The temperature was increased until the reactor exit C<sub>2</sub>H<sub>4</sub> levels reached 97% conversion. The CO level was then  
 15 reduced by a mass flow controller to 100 ppm. Test results are summarized in Table II.

Table II

Catalyst	Comparative Example 2		Example 7	
Pre-reduced	No		Yes	
CO level (ppm)	247	100	247	100
Temperature to reach ~97% conv. (°C)	43		44	
Conversion	98.1	Run-away	96.3	99.6
Selectivity @97% Conversion	-5.7	Run-away	29.9	-146.9

20

The catalyst of Example 7 showed enhanced selectivity  
 25 over the commercially available catalyst of Comparative Example 2. Thus the catalyst of the invention is more tolerant to CO reduction.

5       The principles, preferred embodiments, and modes of  
operation of the present invention have been described in  
the foregoing specification. The invention which is  
intended to be protected herein, however, is not to be  
construed or limited to the particular terms of  
10 disclosure, as these are to be regarded as being  
illustrative, rather than restrictive. Variations and  
changes may be made by those skilled in the art without  
departing from the invention.